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Foamable gel composition

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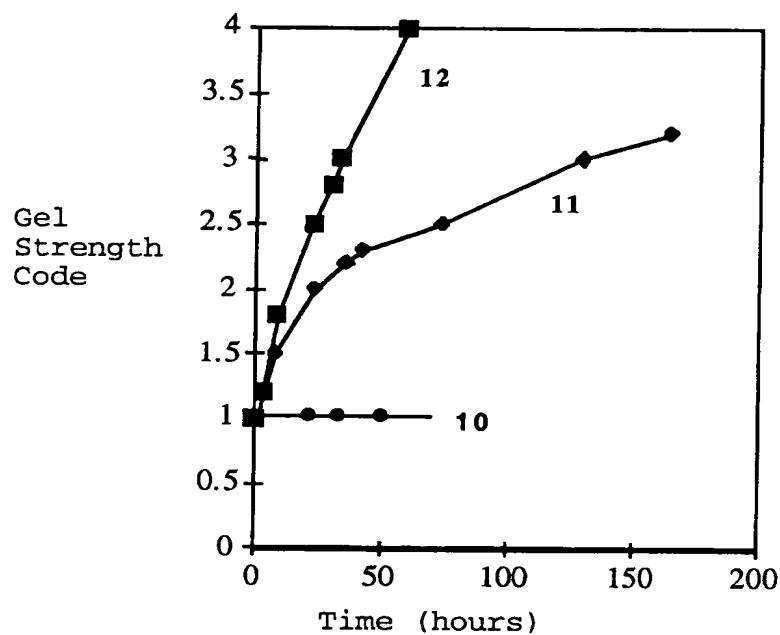
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FIG. 1



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Foamable gel composition

The present invention relates to a foamable gel composition
5 utilized for improving the production of subterranean hydrocarbon reservoirs. More specifically it relates to a gel foamable by a gas containing carbon dioxide. Even more specifically it pertains to a CO₂-foamable gel composition used for conformance control.

10

BACKGROUND OF THE INVENTION

The injection of displacement fluids into subterranean hydrocarbon-bearing formations to promote the production of
15 hydrocarbons therefrom is well known. Water and various gases, in addition to more complex fluids, such as surfactant solutions and polymer solutions, are common displacement fluids utilized in both miscible and immiscible oil displacement floods.

20 When a displacement fluid is injected into a formation has high and low permeability flow paths, the fluid be substantially diverted away from the low permeability flow paths. As a consequence, the displacement fluid does not sweep the low permeability flow paths and the sweep efficiency of the
25 displacement fluid in the formation is poor. Conformance control techniques are employed to improve the sweep efficiency on a macroscopic scale, i.e., by effectively blocking the high permeability flow paths, such as fissure/fracture networks.

30 Polymer gels have been widely used for conformance control of naturally fissured/fractured reservoirs. For an overview of existing polymer compositions, reference is made to the United States patent Nos. 5,486,312 and 5,203,834 which also list a number of patents and other sources related to gel-forming
35 polymers.

In an effort to reduce the cost of the gelling system without substantially diminishing the effectiveness of the treatment,

attempts are known to at least partially substitute the polymer by a less expensive component. One way, which is of specific interest with regard to the present invention, are foamable gel compositions as described for example in the United States patent 5 Nos. 5,105,884, 5,203,834, and 5,513,705, wherein the polymer content is reduced at constant volume of the composition.

The typical components of a foamable gel composition are (a) a solvent, (b) a crosslinkable polymer, (c) a crosslinking agent 10 capable of crosslinking the polymer, (d) a surfactant to reduce the surface tension between the solvent and the gas, and (e) the foaming gas, itself.

United States patent No. 5,105,884 describes foamed gel systems 15 based on partially hydrolyzed polyacrylamide PHPA crosslinked with Cr(III) acetate. With regard to the foaming gas, all four exemplatory systems employ nitrogen (N_2), though CO_2 is mentioned as an alternative.

20 The use of CO_2 as foaming gas is desirable from an economic viewpoint, as this gas is used in many gas injection projects designed to generate an external fluid drive in the reservoir. Therefore an economic source of CO_2 would in principle be available for the gel foaming step. However, experiments with known gel 25 systems showed that CO_2 , when used as foaming gas has a considerable impact on the stability of the gelling system. In contrast to N_2 , CO_2 exhibits significant solubility in both water and oil. When CO_2 dissolves in water, it is converted to carbonic acid. It was found that known formulations for gelling systems either failed to gel 30 in the presence of CO_2 gas or resulted in a gel with reduced long-term stability.

It is therefore an object of the invention to provide a CO_2 , 35 foamable gelling composition. It is a particular object of the invention to provide a cost-efficient composition with sufficient long-term stability to be useable in conformance control applications.

SUMMARY OF THE INVENTION

The above-mentioned objects are achieved by a CO₂-foamable
5 gelling system as set forth in the appended independent claims.

According to the invention, the new gelling system comprises a component which decomposes under downhole conditions to release bicarbonate.

10 Particularly suitable decomposing agents for the purpose of the present invention are urea or derivatives of urea, sodium cyanate, and mixtures, thereof. In a preferred embodiment of the invention, the decomposing agent is chosen so as to stabilize the
15 pH of the gelling system between 4 and 4.5.

From the numerous polymers known to provide a stable gel, it was found that water soluble polyacrylamide (PA) in combination with a Cr(III) based crosslinking agent can be used with particular
20 advantage. In a preferred embodiment, partially hydrolyzed polyacrylamide (PHPA), even more preferably PHPA with an initial degree of hydrolysis in the range of 0.1-2.5%, is used as gelling polymer.

25 It was further found that in contrast to the nitrogen-foamed gelling system as described for example in United States patent No. 5,105,884, the CO₂ gas has a strong and often detrimental impact on the effectiveness of the surfactant in the gelation process. As a result of the failure of most of the known
30 surfactants, a preferred embodiment of the invention comprises alcohol ether sulphates (AES) as surfactant. Alcohol ether sulphates provide a good foaming performance in acid brines with a broad range of ionic strength and hardness. They allow the liquid phase of the foam to form a strong and robust gel under
35 acid conditions.

These and other features of the invention, preferred embodiments and variants thereof, possible applications and advantages will

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become appreciated and understood by those skilled in the art from the detailed description and drawings following hereinbelow.

5

DRAWING

FIG. 1 shows the gel strength of a gelling composition in accordance with the invention in dependence of the amount of added decomposing agent (urea).

10

EXAMPLES

- 15 Measured data showed that CO₂ dissolution can reduce the equilibrium pH of a brine so that it is below a critical gelation pH for the CO₂-foamed gelling composition. Below the critical gelation pH the composition fails to gel. For the the preferred PHPA/Cr(III)/AES system, the critical gelation pH is 4 - 4.5,
20 whereas the CO₂ gas reduces the pH to under 4 - a value which varies depending on the bicarbonate content of the brine.

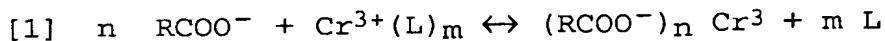
Since the bicarbonate content of typical formation brines can vary in the range 0.0002 - 0.18 mol/l, an internal buffer is required
25 to ensure that the preferred system forms a robust and competent gel under a broad range of reservoir conditions. One method to ensure that the downhole pH is above the critical gelation pH is to add bicarbonate to the mixwater. In practice, this approach is difficult to implement. The addition of bicarbonate (sodium or
30 ammonium salt) to a typical formation brine at surface is likely to cause precipitation of insoluble carbonates such as calcite. More importantly, the addition of Cr(III)carboxylate crosslinker to the bicarbonate-rich brine is likely to cause the precipitation of Cr(III)carbonate so that the Cr(III) concentration in solution
35 is too low to form the gel.

An alternative method to control downhole pH, without causing precipitation at surface, is to add the salt of a weak acid to the

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brine. Examples are formate or acetate (sodium or ammonium salt). In practice, this approach is also unsuitable as a large excess of carboxylate ligands, L, inhibits gelation by shifting the equilibrium:

5



The method used to ensure that the downhole pH is above the critical gelation pH is to add a readily soluble compound which 10 is unreactive at surface but which subsequently decomposes, under downhole pressure and temperature conditions, to release the required pH buffer. Examples which decompose to form the bicarbonate buffer are urea (carbamide) and derivatives of urea such as 1,3-dimethyl urea. Under acid conditions, urea decomposes 15 via the reaction:



The rate of this reaction depends on temperature such that urea 20 is stable at typical surface temperatures but decomposes to release the bicarbonate buffer when the temperature increases above 120 °F. For situations where a controlled release of the buffer is required at lower temperatures (<120 °F), sodium cyanate or a sodium cyanate/urea mixture can be used.

25

A transparent high pressure cell was used to test the performance of the controlled release buffer system under typical reservoir conditions. As a control, a system containing 7 g/l polymer (DH=1%), 127 ppm Cr(III)acetate and 0.5wt% AES (prepared in the 30 brine containing 29800 ppm NaCl, 1250 ppm HCO₃⁻ and 1040 ppm Ca⁺⁺) was aged at P(CO₂)=2000 psi [13.8 MPa] and T=160°F. In accordance with the measurements described hereinbefore, this system did not form a gel as its pH (estimated to be 3.75) is below the critical gelation pH. With urea, in a concentration of 3 g/l (curve 11) 35 and 15 g/l (curve 12), respectively, is added to the same system, under the same gas (CO₂) pressure and temperature conditions, the fluid evolves to form a crosslinked gel (see Fig. 1). The gel

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strength in Fig. 1 is measured in index numbers. A gel strength of above 4 for a period exceeding 1000h is desirable for conformance control applications. The figure also demonstrates that the decomposition rate of the urea increases with initial urea
5 concentration.

It is also possible to replace the urea in the aforementioned example by an equivalent amount, i.e., 4.4 g/l of dimethylurea (DMU), or 6.5 g/l of sodium cyanate. The latter example is
10 advantageously applicable under low temperature conditions. In further examples, the crosslinking agent is replaced by an equivalent amount of Cr(III)propionate.

Furthermore, coreflood experiments were performed to confirm the
15 importance of the decomposing agent.

Two sandpacks (each 1 foot in length and 1 inch in diameter) were initially saturated with the brine containing 29800 ppm NaCl, 1250 ppm HCO₃⁻ and 1040 ppm Ca⁺⁺; the measured brine permeability of both
20 packs was 16 Darcy. At P(CO₂)=2000 psi [13.8 MPa] and T=160°F, a 92vol% CO₂/8vol% brine mixture was then coinjected through each pack; at steady state conditions, the brine saturation was reduced to 40vol% of the pore space in both packs. A 92vol% CO₂/8vol% foam-gel mixture was then coinjected through each pack. The liquid
25 phase of the foam loaded into both sandpacks contained 7g/l PHPA with DH 1-2%, 0.56g/l Cr(Ac)₃, 0.5wt% AES in the brine containing 29800 ppm NaCl, 1250 ppm HCO₃⁻ and 1040 ppm Ca⁺⁺. Coinjection of the CO₂/foam-gel mixture generates a foam which becomes evenly distributed throughout the pore space. A controlled release buffer
30 component was not included in the liquid phase of the foam loaded into Pack 1; as a result, the in-situ pH of the liquid phase of this foam dropped to approximately 3.7, i.e., below the critical gelation pH of the system. A controlled release buffer component (urea) was included in the liquid phase of the foam loaded into
35 Pack 2; the urea increases the bicarbonate concentration in the liquid phase of the foam by 0.05 mol/l so that the in-situ pH of the system stabilized at approximately 4.5, i.e., above the critical gelation pH of the system. After 400 hours aging, the

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flow resistance of the foam/foamed gel in Packs 1 and 2 was measured by injecting the 80vol% CO₂/20vol% brine mixture at a series of constant pressures. A resistance factor (RF), defined by the ratio of the permeability of the pack before and after the 5 foamed gel treatment, is computed at each applied pressure gradient. The measured resistance factors as a function of applied pressure gradient and the critical (failure) pressure gradient for both systems are given in the following table.

10 TABLE 1

	<u>Pressure Gradient</u> in psi/ft [Mpa/m]	<u>Flow resistance (RF)</u> <u>+ urea</u>	<u>-urea</u>
15	10 [0.23]	6667	breakthrough
	50 [1.13]	6667	-
	70 [1.61]	10000	-
	75 [1.72]	10000	-
	80 [1.84]	10000	-
20	110 [2.53]	1429 (breakthrough)	-
	120 [2.76]	500	-

The system containing the decomposing urea creates a competent 25 foamed gel barrier which has a critical (failure) pressure gradient of 110 psi/ft [2.53 MPa/m]. In contrast, the lower pH system without the decomposing agent does not develop a competent foamed gel so that the 80vol% CO₂/20vol% brine mixture penetrates the pack at the lowest applied pressure gradient (10 psi/ft) [0.23 30 MPa/m].

A further example underlines the importance of using a partially hydrolyzed polyacrylamide polymer with an initial degree of hydrolysis in the range 0.1-2.5% in the preferred CO₂-foamed 35 system.

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In a procedure similar to the one described before and under equal pH conditions, two sandpacks (each 1 foot in length and 1 inch in diameter) were initially saturated with the brine containing 29800 ppm NaCl, 1250 ppm HCO_3^- and 1040 ppm Ca^{++} ; the measured brine permeability of both packs was 16 Darcy. Under the conditions $P(\text{CO}_2)=2000$ psi [13.8 MPa] and $T=160^{\circ}\text{F}$, a 92vol% $\text{CO}_2/8\text{vol\%}$ brine mixture was then coinjected through each pack. At steady state conditions, the brine saturation was reduced to 40vol% of the pore space in both packs. A 92vol% $\text{CO}_2/8\text{vol\%}$ foam-gel mixture was then coinjected through each pack; the foam-gel liquid phase contained 7g/l polymer (DH 10-12%), 0.35g/l $\text{Cr}(\text{Ac})_3$ and 1wt% AES. Coinjection of the $\text{CO}_2/\text{foam-gel}$ mixture generates a foam which becomes evenly distributed throughout the pore space. After foam injection, the in-situ gas content of the foam in Pack 1 and Pack 2 was 80vol% and 70vol%, respectively. With time the in-situ foam evolves to form a foamed gel. For each pack, the flow resistance of the foamed gel was measured by injecting the 92vol% $\text{CO}_2/8\text{vol\%}$ brine mixture at a series of constant pressures. At a critical applied pressure gradient, the foamed gel fails allowing the gas and/or liquid to breakthrough the pack. As before, a resistance factor (RF), defined by the ratio of the permeability of the pack before and after the foamed gel treatment, is computed at each applied pressure gradient.

In the present example, the flow resistance of Pack 1 and Pack 2 was measured after aging the in-situ foam for 19.5 and 46.5 hours, respectively. The data are given in Table 2.

30

35

TABLE 2

	<u>Pressure Gradient</u>	<u>Flow resistance (RF) after</u>	
		<u>19.5 h</u>	<u>46.5 h</u>
5	in psi/ft [Mpa/m]		
	1 [0.023]	-	141
	2.5 [0.058]	-	3.2
	6 [0.14]	-	breakthrough
10	20-30	180000	-
	[0.46-0.69]		
	40-50	316000	-
	[0.92-1.15]		
	53 [1.219]	(breakthrough)	-

15

After 19.5 hours, the freshly formed foamed gel imparts a high resistance factor until the applied pressure gradient is increased to 53 psi/ft [1.219 MPa/m]. However, after 46.5 hours, the foamed gel has weakened under the prevailing acid conditions such that it fails at an applied pressure gradient of 6 psi/ft [0.14 MPa/m]. These experiments confirm that for a CO₂-foamed system it is advantageous to use based a polymer with a degree of hydrolysis below 10%.

25 Other measurements performed on unfoamed gelling systems with PHPA of 10-12% indicated that, after the rapid initial formation of a strong gel, the gel subsequently degrades under the prevailing acid conditions.

30 A further example compares the gelation behaviour of five different formulations, containing four different surfactants, all of which are chemically compatible with a PHPA/Cr(III) based gelling system. (Chemical incompatibility is diagnosed by the development of a turbid solution and/or significant

35 precipitation.) The surfactant are the preferred alcohol ether sulfate(AES), a mixed alkyl sulphonate surfactant (MAS) and two different high cloud point non-ionic surfactants (NI1 and NI2)). Details of the formulations are given below in Table 3:

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TABLE 3:

SURFACTANT	AES	MAS	MAS	NI1	NI2
5 CONCENTRATION (in wt%)	0.5	0.25	0.5	0.5	0.5
[Cr(III)] (in ppm)	127	127	260	127	127

10 All formulations were based on 7 g/l PHPA (DH=1%); pH 4.50+/-0.05;
T = 160 °F ; brine containing 29800 ppm NaCl, 1250 ppm HCO₃⁻ and
1040 ppm Ca⁺⁺.

15 Both the non-ionic surfactants (NI1 and NI2) completely inhibit
gelation of the system. The mixed alkyl sulphonate surfactant
causes a long gelation delay (even when the crosslinker/surfactant
ratio in the fluid is twice that in the fluids containing AES) and
when fully formed, the MAS gels are significantly weaker (with a
20 gel strength of 3 using the same definition as introduced with
respect to FIG. 1 hereinbefore) than those formed from the fluids
containing AES (gel strength 5-6).

25 In a further example in accordance with the invention the
Cr(III)acetate was mixed with sodium lactate yielding a more
delayed conversion of the foam to a foamed gel.

CLAIMS

1. Gelling composition for a conformance control operation in a
5 subterranean zone penetrated by at least one borehole, said
composition being foamable with CO₂ gas and comprising
- a water soluble polymer comprising 0.1-2.5 per cent of
carboxylate sidegroups;
- a crosslinking agent
10 - a surfactant; and
- a decomposing agent releasing bicarbonates under
subterranean conditions.
2. The composition of claim 1, wherein the decomposing agents
15 comprises urea or derivatives, thereof.
3. The composition of claim 1, wherein the decomposing agents
comprises sodium cyanate or a mixture comprising sodium
cyanate and/or urea or derivatives, thereof.
20
4. The composition of claim 1, wherein the decomposing agent is
selected so as to produce a pH of 4 - 4.5 in the subterranean
zone.
- 25 5. The composition of claim 1, wherein the polymer comprises
carboxylate sidegroups.
6. The composition of claim 1, wherein the polymer comprises 0.1-
2.5 per cent of hydrolyzed carboxylate sidegroups.
- 30 7. The composition of claim 1, wherein the polymer comprises
polyacrylamide.
8. The composition of claim 1, wherein the surfactant comprises
35 alcohol ether sulfates.
9. The composition of claim 1, wherein the crosslinking agent
is based on Cr(III).

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10. Method of controlling the conformance in a producing wellbore, including the step of injecting a driving fluid through an injector wellbore, characterized in that
- a gelling composition in accordance with claim 1 is provided;
 - said composition is foamed using CO₂; and
 - injected into a subterranean formation through said injector wellbore to block high permeability zones; and
 - injection of said driving fluid is resumed.